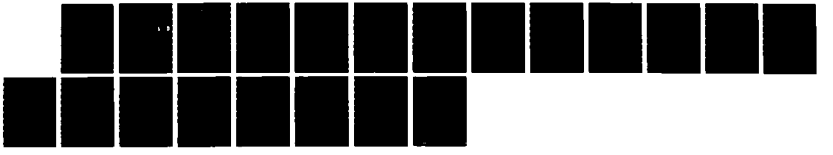
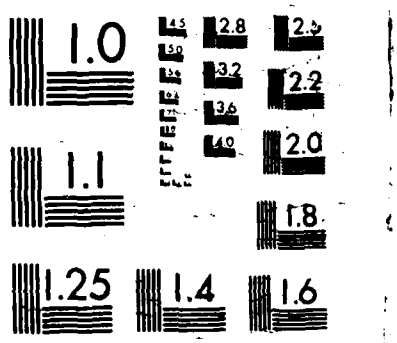
AD-A175 994 DYNAMIC MEASUREMENT OF ULTRAMICRO AMOUNTS OF GASES WITH IONIZATION GAUGE(U) AEROSPACE CORP EL SEGUNDO CA MATERIALS SCIENCES LAB W M GRAVEN ET AL. 16 MAY 83 1/1

UNCLASSIFIED SD-TR-83-39 F04701-82-C-0083 F/G 7/4 NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.8
3.2
3.6
4.0
4.5
5.0

REPORT SD-TR-83-39

Dynamic Measurement of Ultramicro Amounts of Gases with an Ionization Gauge

DTIC
ELECTE
JAN 16 1987
S D
D

W. M. GRAVEN and D. E. GILMARTIN
Materials Sciences Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

AD-A175 994

16 May 1983

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

LIBRARY COPY
JUL 13 1983
LANGLEY RESEARCH CENTER
LIBRARY, NASA
HAMPTON, VIRGINIA

Prepared for

SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

87 1 15 062

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SD-TR-83-39	2. GOVT ACCESSION NO. AD-A175 994	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DYNAMIC MEASUREMENT OF ULTRAMICRO AMOUNTS OF GASES WITH AN IONIZATION GAUGE		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER TR-0083(3935-03)-1
7. AUTHOR(s) Wendell M. Graven and Donald E. Gilmartin		8. CONTRACT OR GRANT NUMBER(s) F04701-82-C-0083
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, California 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Air Force Systems Command Los Angeles, Calif. 90009		12. REPORT DATE 16 May 1983
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Calibrated Gas Leak	Dynamic Instrument Calibration
Ionization Gauge	Mass Spectrometer
Residual Gas Analysis	Traveling-Wave Tube Amplifier
Ultrahigh Vacuum	Ultramicro Gas Measurement

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A nude ionization gauge adjacent to the closed ion-source chamber of a quadrupole mass spectrometer is a sensitive detector of the total amount of gas introduced for dynamic analysis. Linear relations between the amount of gas and the area of the ionization gauge pulse record were found for 8 gases. For relatively unreactive gases, linearity extended to the smallest samples that could be detected, approximately 10^{-10} atm cm^3.

DD FORM 1473 (FACSIMILE)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

Validity of the dynamic method of analysis was established by demonstrating that the same response was obtained for pulsed and for continuous sample introductions from calibrated leak sources of each of the 8 gases.

CONTENTS

I. INTRODUCTION..... 3

II. APPARATUS AND METHOD..... 5

III. RESULTS..... 7

REFERENCES..... 17

DTIC COPY INSPECTED

Accesion For
NTIS CRA&I
DTIC TAB
Unannounced
Justification
By
Distribution /
Availability Codes
Dist | Avail and / or Special
A-1

FIGURES

1. Ionization Gauge and RGA Determinations of Methane Showing Pulse-Shape Retention over a 5-Decade Range of Sample Sizes..... 8

2. Calibrations of RGA and Ionization Gauge for Methane Showing Linearity over a 6-Decade Range of Sample Sizes..... 9

3. Ionization Gauge Calibrations with Several Different Gases..... 11

4. Ionization Gauge Determination of Methane in Accumulated Sample and Effluent from Calibrated Leak..... 12

TABLE

1. Ionization Gauge Responses for Different Gases Introduced as Accumulated Samples or as Effluent from Calibrated Leaks..... 14

I. INTRODUCTION

The purpose of this article is to present a description and results of an unusual application of the standard ionization gauge. The use of a nude Bayard-Alpert ionization gauge to quantitatively measure ultramicro amounts of gases has not been reported to date, and would seem to be infeasible in view of the reported influence of the gauge on the composition of residual gases in an ultrahigh-vacuum system.[1] The results of our investigation, however, demonstrate that several light gases can be measured in amounts as small as 10^{-10} atm cm^3. Applicability of the method is not restricted to the rare gases, but for the more reactive light gases the useful range of the method is limited.

From among the myriad articles on the characteristics and utilization of the ionization gauge, we have selected as references several that relate directly to aspects of our application. For pressure measurements in the ultrahigh-vacuum range, the standard Bayard-Alpert ionization gauge is universally used.[2] With corrections of gauge readings for residual currents, linear calibration curves extending down to about 5×10^{-12} Torr have been reported.[3] The processes that cause a low-pressure limit of measurements with hot-filament ionization gauges have been identified,[4] and the very-rapid response of an ionization gauge to transient gas pressures has been demonstrated.[5] A nude ionization gauge has been used to measure pulsed changes in vapor density, but as the purpose at that time was to monitor and control evaporation rates, the absolute amounts were not determined.[6]

In the process of developing a method for analyzing ultramicro amounts of residual gases in microwave amplifier tubes, it was discovered that the nude ionization gauge in the manifold of the mass spectrometer functioned as a sensitive detector of the total amount of gas introduced for analysis. The devices to be analyzed were production hardware of such size and construction that they required external adaptation so that the residual gases could be transported to the analytical instrument. Because the minimum amounts of gases expected were of the order of 10^{-10} atm cm^3, corresponding to pressures

of 10^{-9} Torr in the devices, transferring of the gas to the mass spectrometer was practicable only if the vacuum system pressure was of the order of 10^{-11} Torr. In order to minimize problems of interaction of the gases with wall and component surfaces, a dynamic method of analysis was developed.[7] The gas was introduced directly into the closed ion-source chamber of the mass spectrometer that was being continuously pumped. Using the fast scanning capability of the instrument, a sufficient number of complete analyses were made to quantitatively characterize the sample before it passed out of the ion-source chamber. The transient response of the ionization gauge was also related to the total amount of gas introduced. The ionization gauge was nearly as sensitive a detector of the total amount of gas as was the mass spectrometer.

II. APPARATUS AND METHOD

Gas analyses were made by means of a quadrupole mass spectrometer built by the Finnigan Corp. The instrument, which consisted of a Series 3200 mass analyzer and a Series 6110 computerized data-handling system, could scan the relevant mass range as rapidly as 5 scans sec^{-1}. Although the operational software was designed for gas chromatographic application, much of it was ideally suited for our dynamic method of analysis.

The all-metal vacuum system was pumped with a 200 ℓ sec^{-1} Ultec ion pump equipped with a titanium sublimator. However, the operational pressure of 10^{-11} Torr was achieved with the use of only the primary ion pump. Two additional 20 ℓ sec^{-1} ion pumps separately pumped the sample inlet and calibration systems. The calibration system contained two gas expansion volumes and a gas sampling volume with approximate volume ratios of 1000:10:1. Provision was also made for interchanging calibrated leaks. With two symmetrically opposed sample inlet systems, gas samples could be introduced through either port directly into the closed ion-source chamber. The introduction of gas was controlled by means of Granville-Phillips Series 203 variable leak valves. The gas entered the ~ 1-cm^3 ion-source volume through 4.5-mm inner diameter (i.d.) tubing; it passed through a 3-mm diameter orifice in order to reach the nude ionization gauge that was mounted on a 5-cm-i.d. flange in the wall of the 9-cm-i.d. manifold. The ionization gauge was mounted in the manifold of the mass spectrometer, adjacent to the closed ion-source chamber. The gas emerging from the ion-source chamber immediately enveloped the nude ionization gauge that measured the total pressure.

The ionization gauge tube was operated at a grid voltage of 180 V. The power to the tungsten filament, which was biased at 30 V, was controlled to maintain a constant grid current of 4 mA. A higher emission current was used for electron bombardment degassing. The gauge controller was an Ultek DGC II which, in addition to the direct digital readout, provided for recording an output analog signal that was directly proportional to measured pressure. This output signal was normally recorded at a chart speed of 1.27 cm sec^{-1}.

Both the ionization gauge tube and the controller were obtained from the Perkin-Elmer Corp.

The reference standards to which all measurements of amounts of gases were related are calibrated gas leaks. Sixteen calibrated leaks of eight different gases were obtained from Teledyne-Hastings-Raydist, and one leak was obtained from Leak Detection Systems, Inc. Leak rates, which ranged from 10^{-6} to 10^{-10} atm cm^3 sec^{-1}, were stated to be accurate to better than ±10% of the calibrated values.

Samples containing known amounts of gas were prepared by accumulating gas from a calibrated leak source in either a 0.05-ℓ or a 5-ℓ volume for a precisely measured time interval, and then isolating an aliquot of the expansion volume in the 4.7-cm^3 sample inlet volume for introduction to the mass spectrometer. These amounts of gas were related to measurements made with a planimeter of the areas traced by the recorded ion gauge outputs, or to the integrated ion intensities of the mass spectrometer in digital counts, after correction for backgrounds.

III. RESULTS

The introduction of a gas sample to the mass spectrometer by opening the variable leak valve resulted in similar time-dependent responses of both the residual gas analyzer (RGA) and the ionization gauge (IG). The manual operation of the variable leak valve controlled the rate of gas introduction, and thereby determined the shape of the response curves. However, the opening operation could be performed in such a way that the shape of the response curves was quite reproducible. Moreover, the shape of the response curves was unchanged over a 5-decade range of the amount of gas introduced. This is demonstrated for methane (CH_4) in Fig. 1, where the RGA and IG response curves are shown as histograms and continuous curves, respectively.

It is apparent that an amount of CH_4 as small as 10^{-10} atm cm^3 can be measured by means of either the RGA or the IG. A pulse-width variation from 3.4 to 5.0 s does not correlate with sample size. Significantly, there are no appreciable differences between the pulse widths of the corresponding RGA and IG response curves. No spreading was observed as the gas pulse passed from the RGA source chamber to the IG. The width of the recorded ion pump current pulse was slightly less than the width of the corresponding IG pulse. In carbon monoxide (CO) desorption studies, Winterbottom[8] also observed a close correspondence of the shapes of the approximately 2-s width pressure pulses measured by the IG and by ion pump current, despite the flow impedance of the intermediate tubulation. He attributed this to a high pumping speed and good conductance of the tubulation in the molecular flow regime.

Areas of the recorded response curves of the IG (Fig. 1) were measured with a planimeter; a linear relationship was found between these areas and the amounts of gas introduced. Similarly, the integrated digital response of the RGA was linearly related to the amount of gas analyzed. The linearity of both relationships extends over the entire 6-decade range that was tested for CH_4, as shown in Fig. 2. The slopes obtained by least squares fit of the full logarithmic data are 0.98 and 0.97 for the RGA and IG data, respectively. It is remarkable that the lower limit of detection of the IG is within a factor

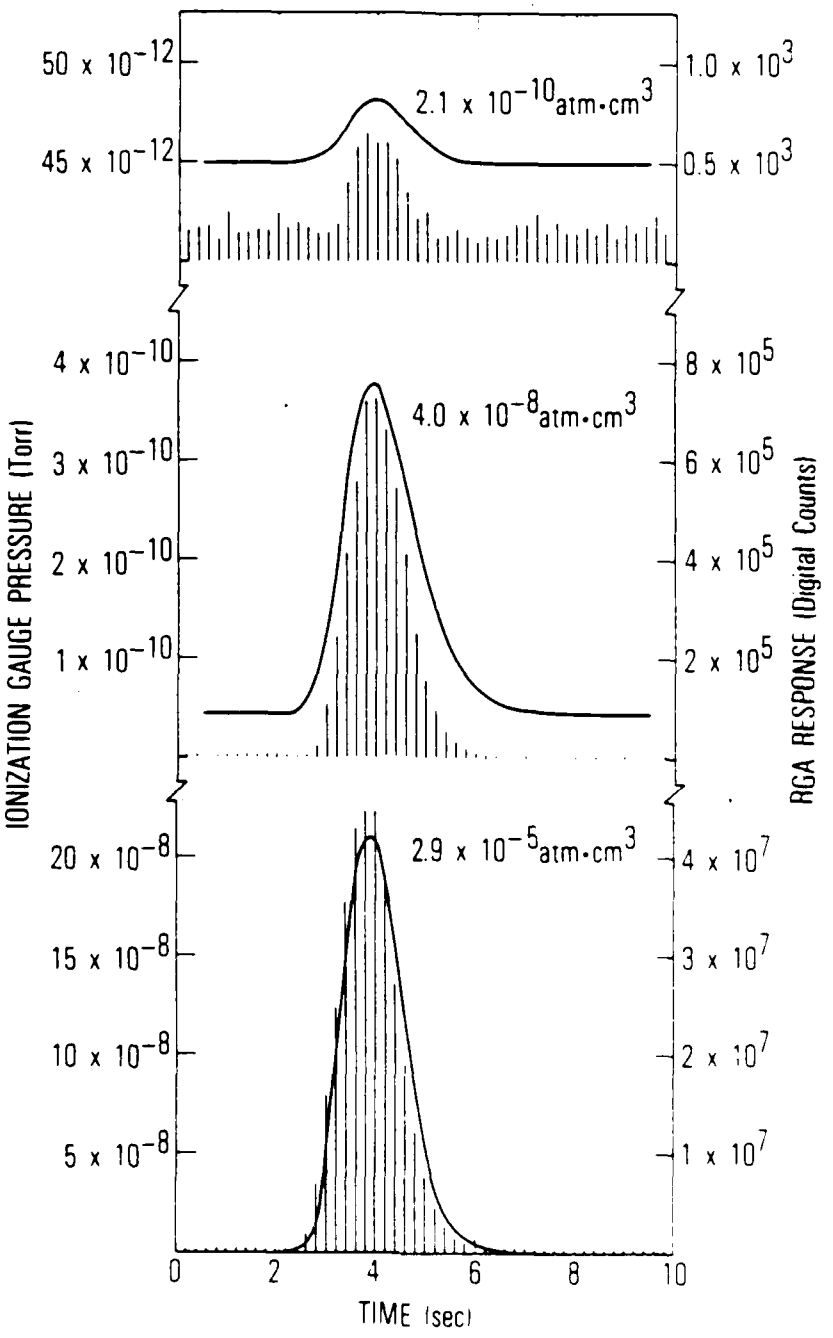


Fig. 1. Ionization Gauge and RGA Determinations of Methane Showing Pulse Shape Retention over a 5-Decade Range of Sample Sizes

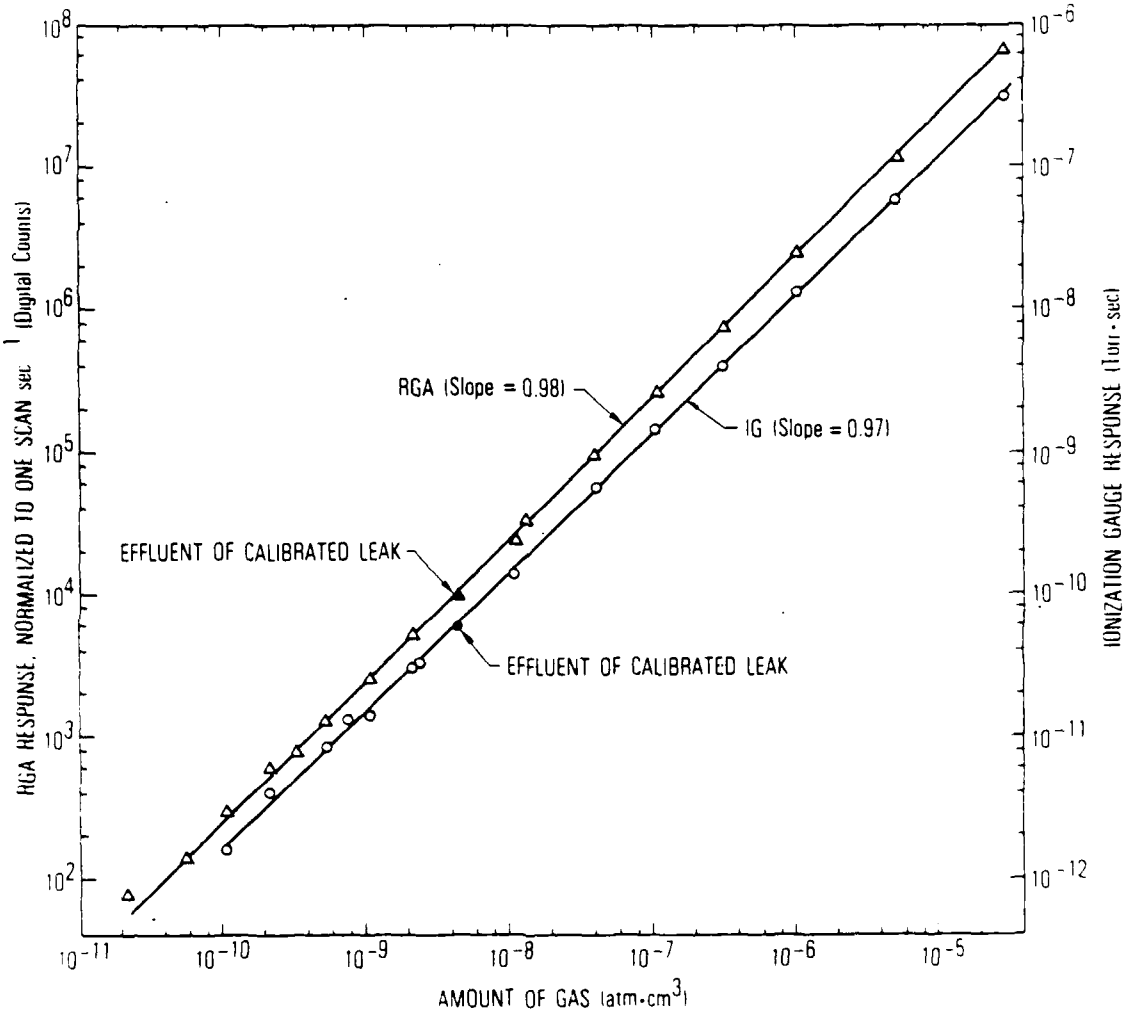


Fig. 2. Calibrations of RGA and Ionization Gauge for Methane Showing Linearity over a 6-Decade Range of Sample Sizes

of 5 of the detection limit of the RGA. The constant sensitivity, indicated by the linearity of response of the IG down to 10^{-10} atm cm^3 of CH_4, is noteworthy in view of the observations of Utterback and Griffith[9] that CH_4 was unsuitable for IG calibration because of chemical interaction.

Results similar to those found for CH_4 were obtained for 7 other gases. However, for CO, carbon dioxide (CO_2), and oxygen (O_2) the detection limits were approximately 10^{-8} atm cm^3. If the larger expansion volume was used, deviations from linearity were observed, indicating that these gases were interacting with the walls of the vacuum system. Of course, the sensitivities of the IG for the different gases were not the same. The linear relationships between IG pulse areas and amounts of gases are shown in Fig. 3 for argon (Ar), nitrogen (N_2), and helium (He). The relative sensitivities for the three gases, obtained from the ordinate intercepts, are in approximate agreement with published results of measurements made under static conditions at much higher pressures.[10]

The IG sensitivities for other gases were obtained from additional measurements that were made to compare the IG responses to a steady flux of gas and to a pulse of accumulated gas. The curve of Fig. 4 illustrates these measurements. In contrast to the procedure used to obtain the data shown in Fig. 1, for the measurement of Fig. 4 the valve to the calibrated leak was left open when the accumulated CH_4 sample was introduced to the RGA. Therefore, when the valve to the RGA was opened the accumulated gas pulse was superimposed on the continuous effluent from the calibrated leak. After the accumulated sample had been pumped away, a constant and reproducible IG pressure (and RGA response, also) resulted from the continuous flow of gas from the calibrated leak. This IG pressure (in Torr) was corrected for the background pressure and normalized to a common calibrated leak rate of 100 atm cm^3 sec^{-1}. Areas of the recorded IG curves (expressed in Torr sec) resulting from introductions of accumulated gas were normalized to a common sample size of 100 atm cm^3.

The two types of IG responses, one obtained by a steady flux of sample and the other by pulses of accumulated samples, are listed for 8 different

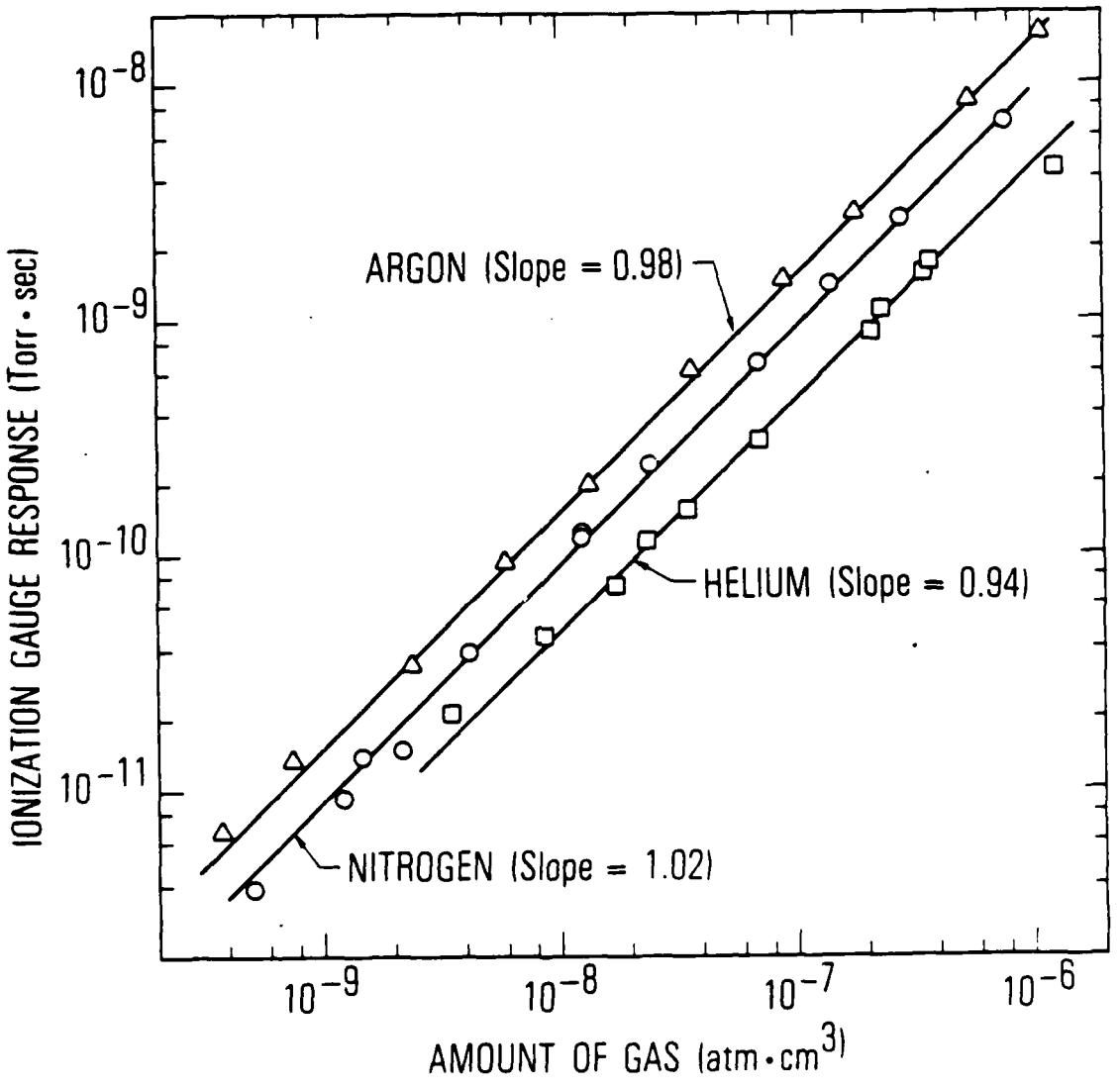


Fig. 3. Ionization Gauge Calibrations with Several Different Gases

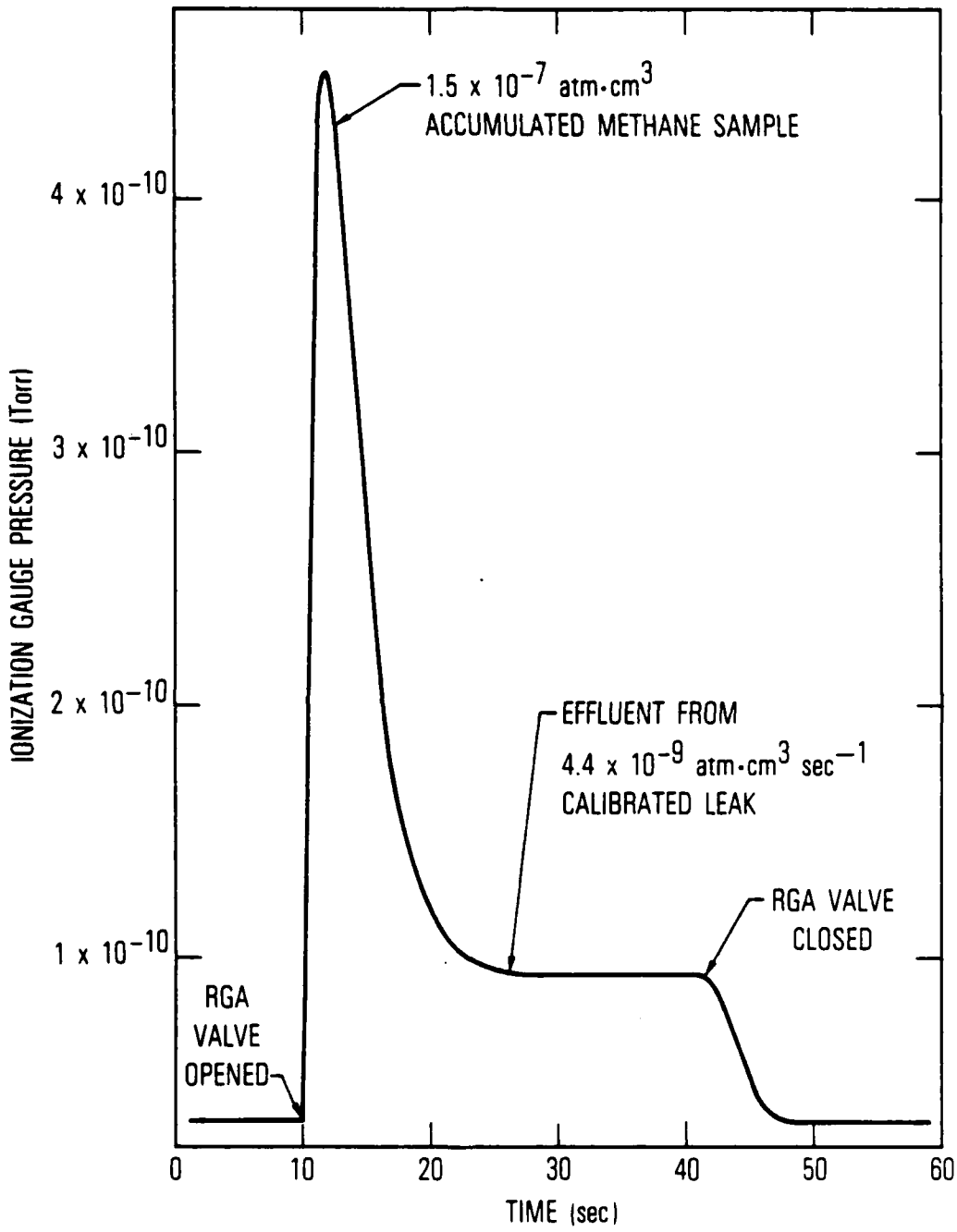


Fig. 4. Ionization Gauge Determination of Methane in Accumulated Sample and Effluent from Calibrated Leak

The two types of IG responses, one obtained by a steady flux of sample and the other by pulses of accumulated samples, are listed for 8 different gases in Table 1. The close agreement between the two sets of IG responses is clear evidence supporting the validity of the dynamic method of measurement. Likewise, close agreement was observed between the two analogous sets of RGA responses.[7] Agreement of the results of IG (and RGA) measurements using both pulsed and continuous introductions of CH_4 is also demonstrated in Fig. 2. The solid points, which were obtained by analysis of the calibrated leak effluent, fit the curves as well as the points corresponding to accumulated samples.

The normalization factor was selected so that the IG responses of Table 1 could be directly compared with published tables of IG relative sensitivities for various gases. Except for somewhat lower responses found for hydrogen (H_2), O_2, and CO, which are known to interact with heated filaments, and a somewhat higher value found for He, the results in Table 1 are in approximate agreement with published relative values obtained from measurements under static conditions at much higher pressures.[10]

The comparative IG response data in Table 1 depend upon the accuracy of the calibrated leak rates. Mason[11] used an analytical mass spectrometer to verify the vendor's calibrations for standard leaks of 6 different gases. His measured leak rates for 5 of the standard leaks were within the vendor's specified accuracy of ±10%, and the difference in leak rates for the other standard leak was 13.5%.

Although no attempt was made in our laboratory to directly confirm the supplier's calibrations, some indirect evidence of their accuracy was obtained. Several calibrated leaks with leak rates differing by at least one decade were available for 6 of the 8 gases; for 2 of the gases, there were 3 calibrated leaks with leak rates that spanned 3 decades. For each gas, all of the calibrated leaks gave quite consistent results. On plots similar to Fig. 2, data points from all the leaks of each gas were fit by the same straight line. Fifteen leaks were constructed and calibrated by one supplier over a period of more than 4 years; one leak was obtained from a second

Table 1. Ionization Gauge Responses for Different Gases Introduced as Accumulated Samples or as Effluent from Calibrated Leaks

	Gauge Responses (10^{-2} Torr sec/atm cm^3)	
Gas	Accumulated Sample	Leak Effluent
Helium	0.45	0.46
Argon	1.47	1.49
Nitrogen	1.02	1.07
Hydrogen	0.14	0.13
Methane	1.36	1.32
Carbon Monoxide	0.43	0.47
Carbon Dioxide	0.91	1.10
Oxygen	0.37	0.39

supplier. It seems almost inconceivable that there could be gross inaccuracies of the calibrations in view of the consistency of the results of our measurements.

REFERENCES

1. P. Repa, Czech. J. Phys. B31, 695 (1981).

2. G. F. Weston, Vacuum 29, 277 (1979).

3. W. D. Davis, J. Vac. Sci. Technol. 5, 23 (1967).

4. J. P. Hobson and P. A. Redhead, J. Vac. Sci. Technol. 2, 93 (1965).

5. J. D. Cobine and E. E. Burger, Rev. Sci. Instrum. 32, 717 (1961).

6. H. Schwarz, Rev. Sci. Instrum. 32, 194 (1961).

7. W. M. Graven and D. E. Gilmartin, Calibration of a Mass Spectrometer for Analysis of Ultramicro Gas Samples Using a Dynamic Method of Analysis, TR-0082(2935-03)-3, The Aerospace Corporation, 16 August 1982. This information was presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI, 6-11 June 1982.

8. W. L. Winterbottom, J. Vac. Sci. Technol. 10, 871 (1973).

9. N. G. Utterback and T. Griffith, Jr., Rev. Sci. Instrum. 37, 866 (1966).

10. P. A. Redhead, J. P. Hobson, and E. V. Kornelsen, Advances in Electronics and Electron Physics, L. Marton, ed., Vol. 17, (Academic Press, New York, 1962), p. 323.

11. T. M. Mason, Instr. and Contr. Systems 43, 73 (1970).

END

2-87

DTIC